Selective Dehydrogenation of 1,3-Cyclohexadiene on Ordered Sn/Pt(111) Surface Alloys

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Abstract: The adsorption and dehydrogenation of 1,3-cyclohexadiene on Pt(111) and two Sn/Pt(111) surface alloys has been studied using TPD, AES, and LEED. The two Pt−Sn surfaces investigated are well-defined, monolayer-thick surface alloys with either a p(2×2) or $(\sqrt{3}\times\sqrt{3})R30°$ LEED pattern and $\Theta_{sn} = 0.25$ or 0.33, respectively. Cyclohexadiene chemisorption on Pt(111) is irreversible and all the chemisorbed monolayer dehydrogenates to form benzene upon heating. Further heating causes most of this benzene product to dehydrogenate completely to form a carbonaceous residue. Some benzene desorbs from the surface at higher coverages. Alloying the Pt surface with Sn completely eliminates the decomposition of benzene without inhibiting the reactivity of cyclohexadiene, dramatically increasing (to 100%) the selectivity of the Pt−Sn surface alloys for gas-phase benzene production. Finally, we observe that the benzene evolution undergoes a stepwise decrease in temperature with increasing Sn concentration and we attribute this to a competition between benzene and hydrogen for adsorption sites.

1. Introduction

The adsorption and dehydrogenation of 1,3-cyclohexadiene on Pt(111) surfaces has been studied previously due to the molecule's possible role as an intermediate in the catalytic conversion of cyclohexane to benzene.[1,2] Studies using bismuth postdosing thermal desorption mass spectroscopy (BPTDS) of this reaction indicate that dehydrogenation of cyclohexadiene occurs at 230−260 K while the benzene product desorbs or dehydrogenates from 300 to 450 K.[2] At low exposures (≤1.1 L), temperature-programmed desorption (TPD) studies did not find a monolayer desorption peak of cyclohexadiene indicating that the dehydrogenation of submonolayer concentrations of cyclohexadiene occurs with unit probability. Furthermore, at these coverages nearly all the benzene produced from this reaction decomposes to form graphitic carbon on the Pt(111) surface. At high coverages gas-phase benzene is produced from cyclohexadiene TPD and two cyclohexadiene desorption peaks are observed at 155 and 175 K which the authors assigned to a multilayer state and a weakly bound chemisorbed state.[2] A shoulder that develops at large exposures in the H_2 TPD spectra at 290 K was assigned to desorption-rate-limited H_2 evolution in this coverage regime. High resolution electron energy loss spectroscopy (HREELS) investigations also indicated quadra-σ-type bonding for 1,3-cyclohexadiene on Pt(111) rather than hydrogen bonding.[2]

The decomposition of hydrocarbons to form carbonaceous or graphitic carbon residue on heterogeneous Pt catalysts is a serious problem for industrial catalysis. This carbon accumulates on the Pt metal surfaces during catalytic reforming and decreases the reactivity of the metal, thus reducing the lifetime of the catalyst. A second metal component, in some cases Sn, is added to Pt catalysts to increase the material's resistance to this carbon buildup or coking.[3−7] These bimetallic catalysts not only have increased coking resistance but also show improved selectivity for producing aromatic hydrocarbons. One interesting question is the importance of alloy formation or direct Pt−Sn interactions to the improvement in catalytic properties observed for the Pt−Sn bimetallic catalysts. This component can be readily addressed using surface science studies of Pt−Sn alloys.

Using two well-defined Sn/Pt(111) surface alloys discovered by Paffett and Windham,[8] we have investigated a number of catalytically interesting hydrocarbon molecules, including ethylene,[9] acetylene,[10] butane and isobutane,[11] isobutylene,[12] cyclohexene,[13] cyclohexane and benzene,[14] and methylcyclohexane,[15] as well as a number of small molecules (CO, H_2, O_2).[16] These studies, as well as studies done on Bi precovered surfaces,[17,18] have shown a significant decrease in the rate of decomposition on the surfaces when low coverages of the second metal species are added to the surface. Specifically, studies of cyclohexene on both of the Sn/Pt alloys[13] and Bi precovered surfaces[18] showed a significant decrease in the dehydrogenation of the benzene produced from the dehydrogenation of cyclohexene and a subsequent increase in the selectivity for these surfaces to produce gas-phase benzene. In this paper we present the results of our investigations of the adsorption and dehydrogenation of 1,3-cyclohexadiene on these Sn/Pt(111) surface alloys using Auger electron spectroscopy (AES), low energy

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electron diffraction (LEED), and TPD. Alloying of Sn in the Pt(111) surface strongly alters the selectivity of cyclohexadiene dehydrogenation on these surfaces: the complete elimination of benzene dehydrogenation causes these surfaces to have 100% selectivity for producing gas-phase benzene from 1,3-cyclohexadiene under UHV conditions.

2. Experimental Methods

The experiments were performed in a stainless steel UHV chamber equipped with instrumentation for AES, LEED, and Ar^+ ion sputtering. A shielded UTI 100C quadrupole mass spectrometer (QMS) was used for TPD. The system base pressure was 5×10^{-11} Torr.

AES spectra were recorded using a Perkin-Elmer (15-255G) cylindrical mirror analyzer (CMA). LEED was carried out using a Perkin-Elmer (15-180) LEED optics. All TPD measurements were made using the QMS in line-of-sight with the sample surface and using a linear heating rate of $\approx$4 K/s. In this procedure, the crystal was positioned $\approx$1 mm from the entry aperture of the QMS shield to reduce contributions to the spectra from the crystal back and edges.[14] A screen biased at −55 V was placed between the QMS and the crystal to eliminate possible damage to the adsorbed layer from low energy electrons coming from the QMS ionizer region.[19]

The Pt(111) crystal could be cooled to 95 K using liquid nitrogen or resistively heated to 1200 K. The temperature was recorded by a chromel−alumel thermocouple spot welded to the side of the crystal. The Pt(111) crystal was cleaned using the procedure found in ref 20.

Preparation of the Pt−Sn surface alloys was achieved by evaporating 1−3 monolayers of Sn on the clean Pt(111) substrate surface followed by annealing the sample to 1000 K for 10 s. Depending upon the initial Sn dose, the annealed surface exhibited either a p(2×2) or $(\sqrt{3}\times\sqrt{3})$-*R*30° LEED pattern.[8] It has now been confirmed that these patterns correspond to the (111) face of a Pt_3Sn alloy and a substitutional alloy of composition Pt_2Sn, respectively, rather than Sn adatoms.[21] Angle-dependent low energy ion scattering spectroscopy (LEISS) measurements using 500−1000 eV of Li^+ showed that the Sn atoms are almost coplanar with the Pt, protruding $\approx 0.022 \pm 0.005$ nm above the surface in a monolayer surface alloy.[21] LEED I−V calculations[22] and X-ray forward scattering[23] have recently confirmed these results. For simplicity the p(2×2) and $(\sqrt{3}\times\sqrt{3})R30°$ Sn/Pt(111) surface alloys will be referred to in this paper as the (2×2) and $\sqrt{3}$ alloys, respectively. A diagram of these surfaces is provided in Figure 1.

1,3-Cyclohexadiene (Aldrich, 97%, [592-57-4]) was purified by freeze−pump−thaw cycles. The purity was checked by in-situ mass spectrometry. Gas exposures for the TPD studies were given with the sample at a temperature below 100 K. Exposures are given in units of Langmuirs (1 L = 10^{-6} Torr·s) after the measured values were multiplied by a factor of 133 to account for the multicapillary array doser enhancement and divided by an additional factor of 6[24] to correct for the ion gauge sensitivity. The doser correction factor was obtained by comparing uptake curves from exposures produced by the directed beam doser with those from background exposures. Because of the carbon contamination resulting from C_6H_8 TPD experiments on clean Pt(111), the surface must be cleaned following each experiment. The carbon contamination was removed by heating the surface to 800 K in 2×10^{-8} Torr of O_2 for 10−15 min and then flash annealing to 1000 K in vacuum. The cleanliness and long-range order of all surfaces were checked using AES and LEED prior to each experiment. In addition, the alloy surfaces were checked with LEED following each TPD experiment to assure no irreversible adsorbate induced reconstruction occurred.

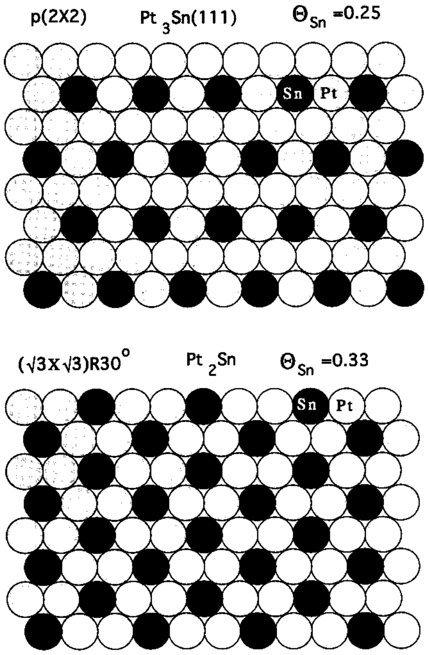

Figure 1. Surface diagram for the p(2×2) and $(\sqrt{3}\times\sqrt{3})R30°$ Pt−Sn surface alloys.

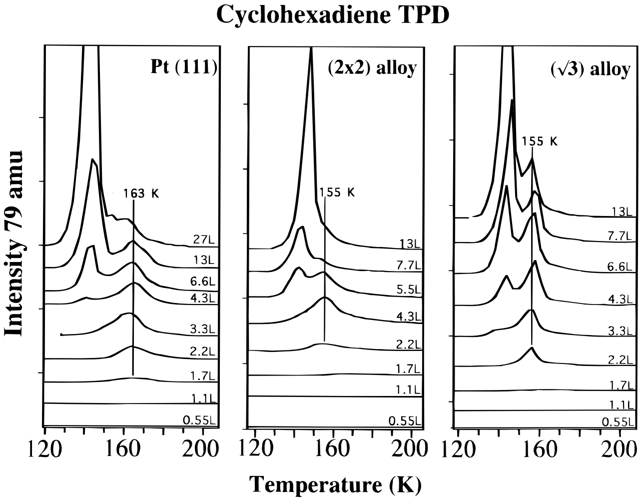

Figure 2. TPD spectra for C_6H_8 desorption on Pt(111) and the (2×2) and $\sqrt{3}$ Pt−Sn surface alloys. No desorption is seen below an exposure of 0.8 L for any of the surfaces. Note that no high temperature state is observed for C_6H_8 desorption on this surface, indicating that the strongly bonded chemisorption state of C_6H_8 has unit probability to undergo dehydrogenation.

3. Results

1. Adsorption and Desorption of 1,3-Cyclohexadiene. The adsorption and desorption behavior of cyclohexadiene was studied primarily with TPD. Some of the data for a series of exposures producing low to high coverages of cyclohexadiene on clean Pt(111) and the two Pt−Sn alloys are shown in Figure 2. Our results on Pt(111) agree well with those obtained by Hugenschmidt et al.,[2] except that our desorption temperatures are shifted down $\approx$10 K. This can be attributed at least partially to the different heating rate used in our studies ($\approx$4 K/s) compared to the variable rate between 9.7 and 5 K/s reported by Hugenschmidt et al.[2] Signals at 80, 79, 78, and 76 amu were observed to monitor for possible gas-phase cyclohexadiene and benzene products and to distinguish any contributions to these spectra from cracking in the QMS. Mass 54 was observed to look for possible C_4 species. Signals at 28, 18, and 2 amu

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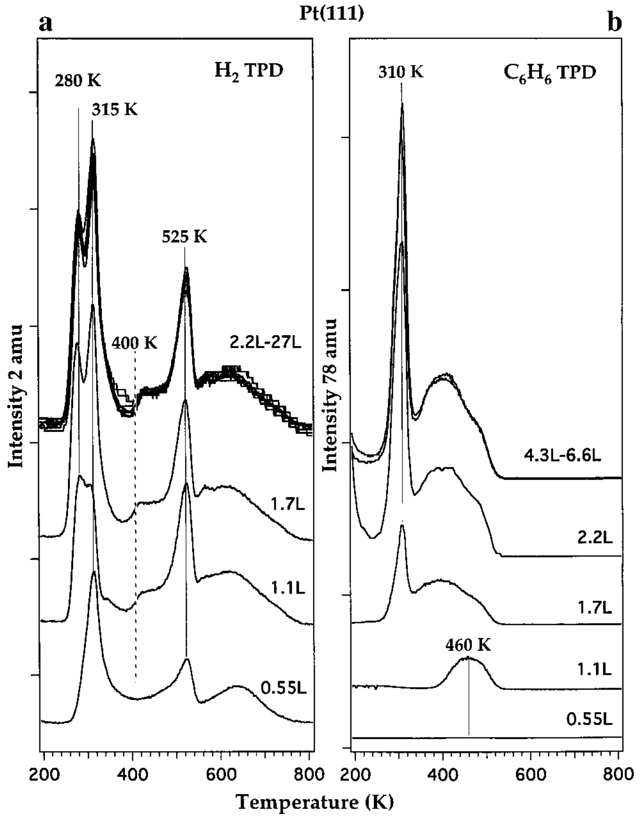

Figure 3. TPD spectra for H_2 and C_6H_6 desorption on Pt(111). (a) Pt(111) shows two regions of H_2 desorption: above 400 K, which is attributed to C_6H_6 decomposition; and below 400 K, which is attributed to C_6H_8 dehydrogenation. (b) On Pt(111) no C_6H_6 desorption is seen until an exposure of ≥0.8 L. C_6H_6 desorbs in two states: a sharp peak at 315 K and a broad peak from 400 to 520 K. C_6H_6 saturates on this surface at an exposure of 2.1 L.

were monitored to measure sample contamination and possible dehydrogenation products. No new desorption features that might indicate a new or intermediate dehydrogenation product were observed at these masses on any of the three surfaces. Signals at 82 and 84 amu were also monitored for possible hydrogenation products. No desorption features for these masses were observed at any temperature or exposure during these studies. These results are in agreement with Hugenschmidt et al.,[2] who found no significant hydrogenation product even after coadsorbing H atoms with adsorbed cyclohexadiene on the surface.

Adsorption kinetics (uptake) plots for cyclohexadiene adsorption on the three surfaces were constructed from the data shown in Figures 2−5. The three surfaces showed no differences in their cyclohexadiene uptake curves. The amount of desorption of H_2 and C_6H_6 increased at a steady rate on all three surfaces until ≈2.1 L where both peaks saturated. A peak due to the physisorbed cyclohexadiene desorption state that is distinct from the multilayer state grew in from a dose of ≈2.1 L to a dose of ≈4.3 L, where it saturated. We can determine from the uptake plots that the coverage of this state is approximately one monolayer and we associate this peak with the first physisorbed layer on top of the chemisorbed monolayer. A multilayer desorption state was observed for exposures larger than 4.3 L that did not saturate up to exposures of over 27 L.

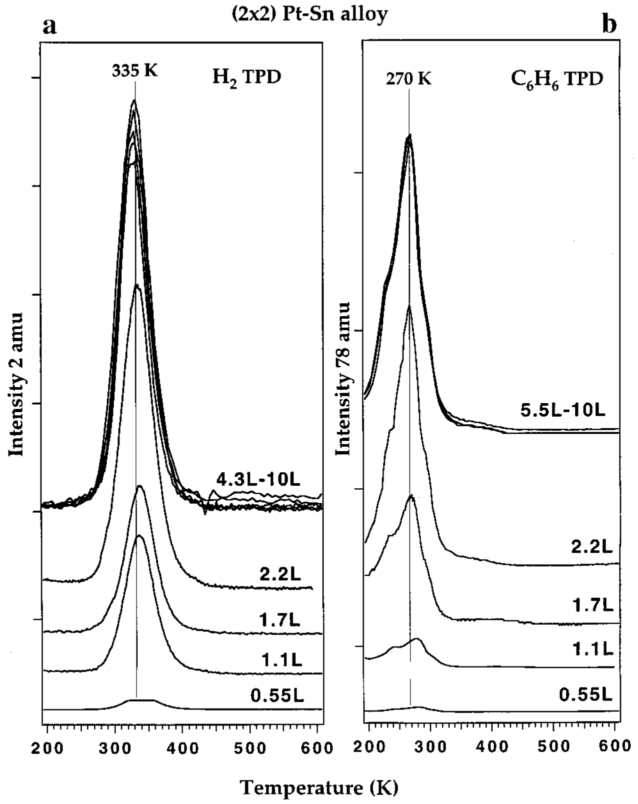

Figure 4. TPD spectra for H_2 and C_6H_6 on the (2×2) Pt−Sn alloy surface. (a) The (2×2) Pt−Sn alloy shows a single H_2 desorption state at 330 K which saturates at 2.1 L. (b) On the (2×2) alloy C_6H_6 desorbs at all coverages in one state at 280 K. Saturation occurs at 2.1 L.

As shown in Figure 2, at exposures below 1.7 L on Pt(111), no molecular cyclohexadiene desorption occurs and all the adsorbed cyclohexadiene dehydrogenates. Increasing the cyclohexadiene exposure first populates a state that desorbs at 180 K. As the exposure is increased the peak temperature shifts down ≈15 K to 165 K and the intensity increases. After an exposure of 4.3 L a new peak at 145 K is observed. This peak cannot be saturated and continues to gain intensity with increasing cyclohexadiene dose. Hugenschmidt et al.[2] previously assigned the peak at 145 K to multilayer desorption and the peak at 165 K to a weakly chemisorbed state where cyclohexadiene is bound in unfavorable sites either between strongly chemisorbed molecules or in a second layer above them. We agree with their assignment of the multilayer state, but we assign the 165−180 K peak to a second, physisorbed layer on top of the chemisorbed monolayer since the amount of cyclohexadiene that desorbs in this state is greater than or equal to one monolayer.

TPD spectra of cyclohexadiene on the (2×2) and $\sqrt{3}$ alloys for increasing exposures are also shown in Figure 2. Cyclohexadiene TPD spectra on the two alloys are nearly identical to that on Pt(111). At low exposures (<1.7 L), no cyclohexadiene desorption is observed. As the exposure is increased two peaks form, one at 155−160 K assigned to the second layer and the multilayer peak with an onset near 130 K and a peak at these coverages near 145 K.

Both alloy surfaces and occasionally the Pt(111) surface also exhibited higher temperature peaks at *m*/*e* 79. However, these peaks were of very low intensity and tracked the benzene desorption peaks exactly. These peaks occurred at the same temperature and in the same intensity ratio as the peaks for benzene desorption and are thus assigned to originate from reactions in the mass spectrometer ionizer.

Cyclohexadiene TPD spectra from the Sn/Pt(111) alloy surfaces, therefore, show no change from the clean Pt(111) surface apart from a slight reduction in desorption activation energy for the second layer desorption peak on the alloys. In our previous study[13] of cyclohexene adsorption on these three

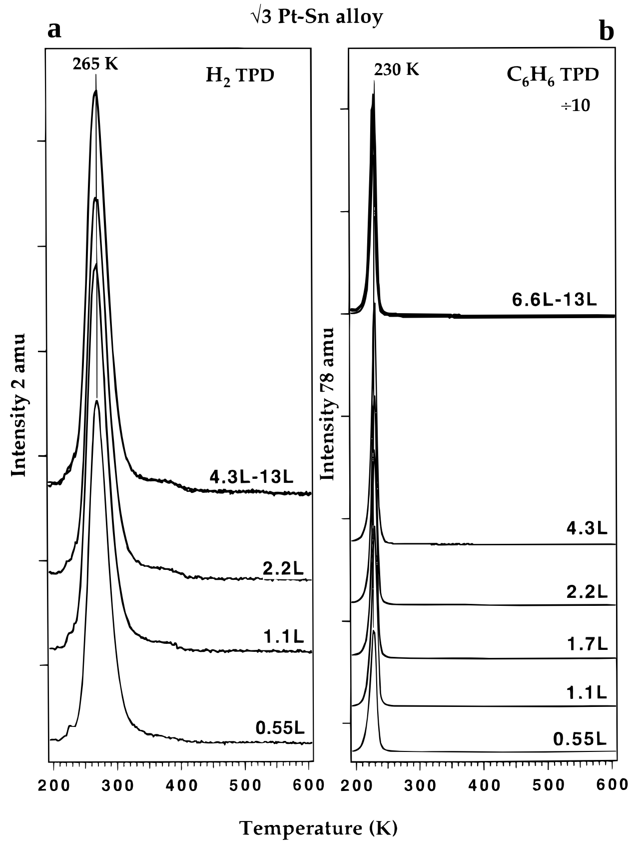

Figure 5. TPD spectra for H_2 and C_6H_6 on the $\sqrt{3}$ Pt−Sn alloy surface. (a) The $\sqrt{3}$ Pt−Sn alloy shows a single H_2 desorption state at 260 K which saturates at 2.1 L. (b) On the $\sqrt{3}$ alloy C_6H_6 desorbs at all coverages in a single state at 225 K.

substrates, peaks corresponding to the chemisorbed cyclohexene monolayer were observed at 200−280 K depending on the concentration of Sn at the surface. The absence of any similar high-temperature states for cyclohexadiene indicates that chemisorbed cyclohexadiene is completely, irreversibly adsorbed on all three surfaces. As we shall see, heating the molecularly chemisorbed monolayer causes dehydrogenation to benzene in all three cases as well.

The monolayer saturation coverage of chemisorbed C_6H_8 was determined by comparing the area under the H_2 TPD curve after a saturation dose of H_2 on Pt(111), to give $\Theta_H = 0.8$,[25−27] to the amount of H_2 evolved from the dehydrogenation of cyclohexadiene to benzene on Pt(111) and the Pt−Sn surface alloys. Using this calibration, we arrive at a coverage of chemisorbed cyclohexadiene of $\Theta_{C_6H_8} = 0.15$ on the $\sqrt{3}$ alloy and $\Theta_{C_6H_8} = 0.14$ on the (2×2) alloy, nearly independent of the presence of Sn in the alloy surfaces. Hugenschmidt et al.[2] previously carried out an independent estimation for the coverage of chemisorbed cyclohexadiene on Pt(111). If the coverage for the onset of benzene desorption on Pt(111) is 0.06 molecules per Pt atom,[17] and the conversion probability for C_6H_8 is ≈100% at this coverage, then the coverage of cyclohexadiene at the exposure required to first produce gas-phase benzene is 0.06 molecules per Pt atom.[2] Assuming that cyclohexadiene coverage is proportional to exposure at low doses yields a saturation coverage of $\Theta_{C_6H_8} = 0.19$.[2] This is in agreement with our study of the adsorption kinetics of cyclohexadiene on the Pt(111) surface that found a saturation coverage for cyclohexadiene of $\Theta_{C_6H_8} = 0.18$. These two independent methods provide estimates in quite reasonable agreement.

We also used LEED in these investigations. Exposing the surface alloys to monolayer coverages of cyclohexadiene, 1.7 L, only caused an increase in the diffuse background intensity for both alloy surfaces. Also the p(2×2) and $(\sqrt{3}\times\sqrt{3})R30°$ LEED patterns were still visible and sharp indicating that the adsorption of cyclohexadiene does not significantly alter the 2-D structure of these surface alloys. Unless cyclohexadiene forms ordered structures with the same size and orientation as the unit cells of the surface alloys, chemisorption occurs into a disordered adlayer phase.

2. Dehydrogenation of 1,3-Cyclohexadiene. TPD spectra showing H_2 and C_6H_6 evolution from the dehydrogenation of adsorbed cyclohexadiene on clean Pt(111) are shown in Figure 3. Our results for H_2 and C_6H_6 from clean Pt(111) agree well with those of Hugenschmidt et al.[2]

At low coverage, 0.55 L, the H_2 desorption occurs in three distinct regions: sharp peaks at 315 and 525 K and a broad region from 550 to 750 K. This spectrum is also very similar to that seen for the dehydrogenation of both cyclohexane and cyclohexene on clean Pt(111).[13,14] Accordingly, we can usefully separate these H_2 TPD spectra into two regions: desorption below 400 K and above 400 K. The region above 400 K appears the same for the dehydrogenation of adsorbed cyclohexane, cyclohexene, cyclohexadiene, and benzene on Pt(111) and has been assigned to the dehydrogenation of benzene to carbon.[2,14] The region below 400 K is due to the dehydrogenation of cyclohexadiene to form adsorbed benzene. Accordingly, the area ratio of the H_2 desorption areas in these two regions provides an accurate measure of the selectivity for producing gas-phase benzene. The ratio ($T > 400$ K/$T < 400$ K) ranges from 3 to 1.7 for 0.55 to 2.1 L, corresponding to 100% and ≈60%, respectively, as the fraction of total benzene that decomposes. Hugenschmidt et al.[2] observed a peak temperature of the H_2 desorption peak from cyclohexadiene dehydrogenation for low coverages to be ≈300 K, and proposed that the H_2 evolution was largely desorption-limited.[2] We agree with this conclusion.

At higher coverages a lower temperature H_2 peak at 280 K develops. This peak most likely corresponds to a shoulder observed by Hugenschmidt et al.[2] at 290 K at high exposures which they assigned to H_2 desorption rate limited H_2 evolution from the Pt(111) surface. This peak is also very similar to the low-temperature H_2 TPD peak seen in the study of cyclohexene dehydrogenation on Pt(111) at large cyclohexene coverages.[13] It appears that two states of hydrogen produced from the dehydrogenation of cyclohexadiene on clean Pt(111) exist, giving rise to a peak at 280 K and one at 315 K. An explanation for these two peaks comes from understanding the coverage dependence of H_2 desorption from the Pt(111) surface. In previous studies of H_2 adsorption on Pt(111), TPD spectra showed that H_2 desorbs from 400 to 280 K after H_2 exposures ranging up to saturation coverage.[28] Thus, coadsorbates can produce repulsive interactions that can easily lower the desorption temperature to 280 K. Given that this range includes both peaks observed in Figure 3 below 400 K, one explanation is that both peaks are H_2 desorption rate-limited, but influenced by the large change in coadsorbate coverage that occurs due to benzene desorption at 310 K. Hydrogen desorbs at 280 K in the presence of the entire amount of coadsorbed benzene produced by the dehydrogenation of cylcohexadiene. But, after desorption of some of the benzene at 310 K, which is also

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destabilized due to coadsorption with hydrogen, the remaining hydrogen desorbs at a slightly higher temperature of 315 K.

H_2 evolution from the (2×2) alloy surface is shown in the left panel of Figure 4. H_2 TPD shows a single peak at 330 K which occurs at the same temperature as H_2 desorption that results from atomic hydrogen dosed to the (2×2) alloy surface.[16] Therefore, this peak is assigned as rate limited by H_2 desorption. Figure 4 also illustrates that there is no H_2 desorption at any coverage above 400 K indicating that the benzene formed from the dehydrogenation of cyclohexadiene no longer undergoes decomposition. This is expected based on our earlier studies of benzene adsorption on Pt−Sn alloys.[13]

As shown in the left panel of Figure 5, H_2 evolution from the dehydrogenation of cyclohexadiene adsorbed onto the $\sqrt{3}$ alloy similarly has a single H_2 TPD peak, but this peak occurs $\approx$70 K lower in temperature at 260 K. This desorption state is also at the same temperature as that observed for desorption of H_2 following H atom dosing to the $\sqrt{3}$ alloy surface and therefore is also assigned to a H_2 desorption rate-limited process.[16] There is no H_2 evolution above 400 K at any dose of cyclohexadiene on the $\sqrt{3}$ alloy. This verifies that the presence of Sn has eliminated the pathway for benzene dehydrogenation on the alloy surfaces.

AES studies indicate that *no carbon is left on the surface following TPD studies on either alloy surface.* This is consistent with the H_2 TPD results. AES spectra following TPD studies of cyclohexadiene on clean Pt(111) show significant amounts of carbon remain on the surface for all coverages of chemisorbed cyclohexadiene.

We now turn our attention to C_6H_6 desorption after cyclohexadiene exposures on clean Pt(111). As Figure 3 shows, no C_6H_6 desorption was seen from the Pt(111) surface for exposures of less than 1.1 L. However, as we will discuss later, Figures 4 and 5 show that C_6H_6 desorption for the two Sn/Pt(111) surface alloys occurred at the lowest exposures we investigated. At higher coverages, we observe in Figure 3 a benzene desorption pulse at 310 K and continued benzene desorption until 500 K. The initial desorption temperature is the same as previously found for benzene desorption following benzene adsorption on clean Pt(111)[14] indicating that benzene desorption is the rate-limiting step for the production of gas-phase benzene from cyclohexadiene dehydrogenation on Pt(111). This result is consistent with BPTDS studies which indicated that cyclohexadiene dehydrogenation occurred at $\approx$230 K.[2] No change in the shape of the benzene TPD spectra is seen at higher cyclohexadiene exposures and a saturation benzene yield is observed at an exposure of 2.2 L. The sharp onset for the pulse of C_6H_6 desorption at 310 K has previously been observed for cyclohexene[13,18] and cyclohexadiene[2] on Pt(111) and was attributed to an autocatalytic process.[2]

Low-temperature peaks at 165 and 145 K were also observed in both the H_2 and C_6H_6 TPD spectra. These peaks were at the identical temperature and in precisely the same peak intensity ratios as those seen for cyclohexadiene desorption at 79 amu. Because they mirror the cyclohexadiene desorption peaks exactly and are at lower intensity we have assigned them to cyclohexadiene cracking fractions.

The C_6H_6 TPD spectra for cyclohexadiene adsorption on the Sn/Pt(111) surface alloys are shown in Figures 4 and 5. Both surface alloys have only a single desorption peak that occurs at temperatures much lower than that seen for C_6H_6 desorption from Pt(111). The C_6H_6 desorption peak from the (2×2) alloy is comprised of features at 230 and 270−280 K. C_6H_6 desorption is observed for all exposures and the desorption yield saturates after 2.2 L cyclohexadiene exposures. The desorption temperature and the peak shape are quite different from that found for the desorption of benzene following benzene adsorption on the (2×2) alloy surface.[14] In the previous benzene experiments, three C_6H_6 desorption peaks were observed on the (2×2) alloy surface, at 200, 280, and 400 K, corresponding to a physisorbed state and two chemisorbed states.[14] Only a peak at 280 K with a small feature at $\approx$230 K was observed in this study which indicates that while gas-phase benzene production is still benzene desorption rate-limited, some benzene adsorption sites must have been eliminated.

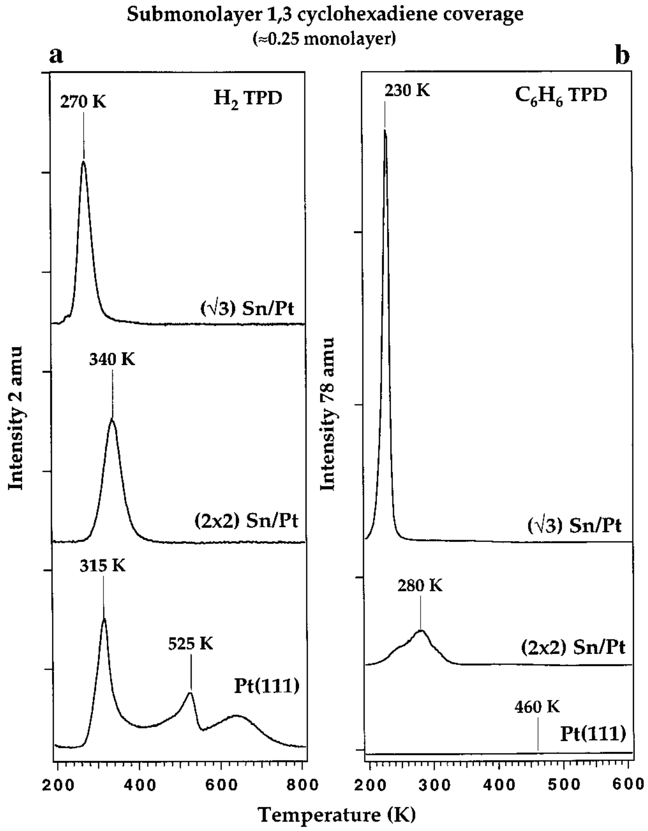

Figure 6. TPD spectra of both C_6H_6 and H_2 on Pt(111) and the Pt−Sn surface alloys at submonolayer coverage ($\approx$25% saturation coverage). This coverage was produced by a dose of 0.55 L. This TPD series was taken carefully ensuring uniform mass spectrometer sensitivity, system pressure, and dosing conditions. (a) H_2 desorption occurs at submonolayer coverages on Pt(111) indicating that despite the absence of C_6H_6 desorption in this coverage regime cyclohexadiene and benzene dehydrogenation still occur. (b) No C_6H_6 desorption occurs at this coverage on the Pt(111) surface. A single desorption state occurs for C_6H_6 on the surface alloys at even the lowest surface exposures.

C_6H_6 desorption from cyclohexadiene dehydrogenation occurs in a single very sharp peak at 225 K on the $\sqrt{3}$ alloy surface. The sharpness of the C_6H_6 peak and its abrupt onset at low coverage is a sign of an autocatalytic process. Also, C_6H_6 desorption occurs $\approx$75 K lower in temperature than would be expected based on our previous study of benzene adsorption on the $\sqrt{3}$ surface alloy, in which two distinct desorption peaks for C_6H_6 were observed at 200 and 300 K.[14] One possibility, in addition to an autocatalytic phenomenon, is that competition for sites between coadsorbed H atoms and benzene reduces the benzene adsorption energy on this surface. Saturation yields for benzene production on the $\sqrt{3}$ surface alloy occur after cyclohexadiene exposures of 2.1 L.

Figures 6 and 7 illustrate more clearly the altered desorption characteristics of both cyclohexadiene dehydrogenation products on the Pt−Sn surface alloys. In these figures we directly compare H_2 and C_6H_6 TPD spectra on Pt(111) and the two alloy

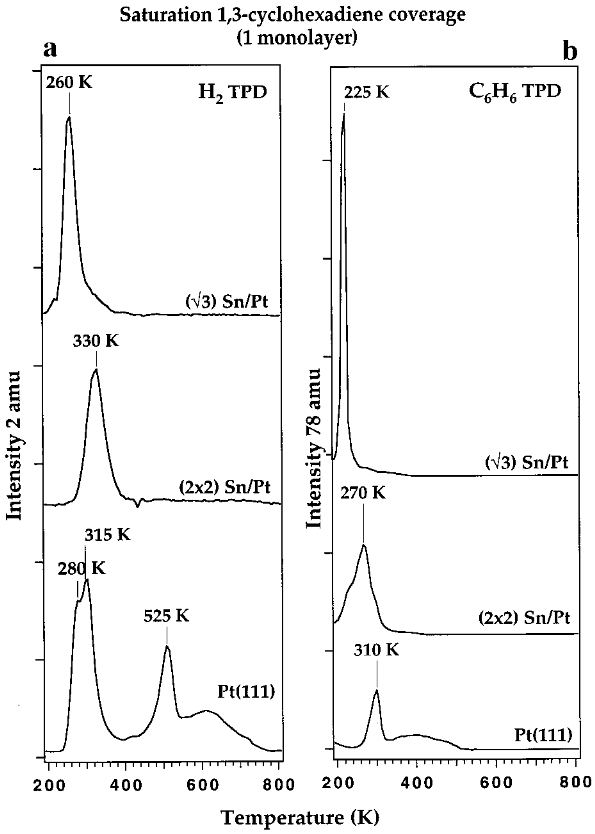

Figure 7. TPD spectra of both C_6H_6 and H_2 on Pt(111) and the Pt−Sn surface alloys at saturation coverage. This coverage was produced by a dose of 4.4 L. This TPD series was taken carefully ensuring uniform mass spectrometer sensitivity, system pressure, and dosing conditions. (a) The H_2 TPD spectra shows the elimination of all H_2 desorption above 400 K on the two Pt−Sn surface alloys. On Pt(111) note two states exist below 400 K: one at 280 K which is assigned to desorption rate-limited H_2 and a state at 300 K attributed to reaction rate-limited H_2. (b) On Pt(111) C_6H_6 desorption occurs from 315 to 520 K. On the (2×2) Pt−Sn surface alloy site-blocking from H atoms reduces this C_6H_6 desorption to two states: one at 280 K and one at 230 K. Site-blocking from both Sn and H atoms on the $\sqrt{3}$ alloy reduces the C_6H_6 desorption to a single physisorbed state at 225 K.

surfaces for the same cyclohexadiene exposures and coverages (since the sticking coefficient at 100 K is a constant). Figure 6 shows results from the reaction of a submonolayer coverage of cyclohexadiene ($\Theta_{C_6H_{10}} = 0.05$ or $\approx{}^1/_4$ of monolayer coverage) and Figure 7 shows monolayer saturation coverage results. These two figures clearly show the stepwise decrease that occurs in the adsorption energies for both H_2 and C_6H_6 as the concentration of Sn is increased from the (2×2) to the $\sqrt{3}$ alloy surfaces. Further, in the submonolayer coverage regime, Figure 6, no gas-phase benzene production was observed from the Pt(111) surface. The absence of gas-phase benzene production at low cyclohexadiene coverages, 0.06 molecules per Pt atom, was also observed by Hugenschmidt et al.,[2] and it has been suggested that in this low coverage regime all the benzene produced on the Pt(111) surface undergoes decomposition. Modifying the cyclohexadiene coverage causes only small alterations in the TPD spectra, as shown in Figure 7. One notable change in the chemistry of the Pt(111) surface at higher coverages is a reduced selectivity for benzene dehydrogenation, resulting in the desorption into the gas phase of some of the benzene product. The decrease in the rate for dehydrogenating benzene at saturation coverage is a consequence of adsorbate induced poisoning of the Pt(111) surface. Also of note in the H_2 TPD plots in both of these figures is the complete elimination of higher temperature H_2 production on the two alloys which indicates that the pathway for dehydrogenating benzene has been shut down on the alloy surfaces.

4. Discussion

4.1. 1,3-Cyclohexadiene Adsorption and Reaction on Pt(111) and Pt−Sn Surface Alloys.

4.1. 1,3-Cyclohexadiene Adsorption and Reaction on Pt(111) and Pt−Sn Surface Alloys. Cyclohexadiene adsorbed onto clean Pt(111) and the two Sn/Pt(111) surface alloys at 100 K desorbs in two peaks: a second layer physisorbed state at 155−165 K depending on the surface and a multilayer state near 145 K on all three surfaces. These cyclohexadiene desorption peaks are only observed after doses of 2.2 L. Below this exposure cyclohexadiene dehydrogenates with unit probability. *Alloyed Sn in the Pt−Sn alloys at either ${}^1/_3$ or ${}^1/_4$ monolayer Sn concentrations does not significantly inhibit the activity of Pt(111) for the dehydrogenation of cyclohexadiene to produce benzene* since no new high-temperature molecular cyclohexadiene desorption peaks are observed on the alloy surfaces. The coverage of chemisorbed cyclohexadiene is nearly independent of the Sn concentration on these surfaces and all three surfaces investigated irreversibly adsorb and completely dehydrogenate the chemisorbed monolayer of cyclohexadiene to produce benzene.

Reaction of the chemisorbed cyclohexadiene monolayer leads to only two desorption products, H_2 and C_6H_6, on Pt(111) and the two surface alloys. The most significant change in the H_2 and C_6H_6 TPD spectra comparing Pt(111) to the alloys is the complete disappearance of H_2 desorption above 400 K and the changing adsorption energy and peak shape for the benzene product on the Pt−Sn surface alloys.

First, let us discuss the chemistry of cyclohexadiene on clean Pt(111). For our purposes, we have divided the H_2 desorption in TPD into two regions after adsorption of cyclohexadiene on Pt(111): above 400 K, and below 400 K. The broad structure from 400 to 800 K in the H_2 TPD spectra has also been observed after adsorption of a number of other hydrocarbon molecules on Pt(111), including cyclohexane,[10,18] cyclohexene,[13,29] and benzene[14,30] in separate studies. This peak structure has been assigned to the complete dehydrogenation of benzene to "graphitic" carbon. This decomposition of benzene indicates that clean Pt(111) is too reactive and therefore not selective in its dehydrogenation of C_6H_8 (and the other mentioned hydrocarbons) and converts a significant amount of the initial concentration of chemisorbed cyclohexadiene into a coking product.

The H_2 peaks evolved below 400 K after cyclohexadiene adsorption on Pt(111) are clearly due to the dehydrogenation of cyclohexadiene to benzene, but an explanation for their profile is less clear. There are two H_2 peaks, one at 315 and one at 280 K. The lower temperature peak at 280 K develops at higher coverages. Now H_2 desorption from H_2 adsorption on the Pt(111) surface occurs in a peak at ≈280 K at saturation coverage, but the desorption activation energy for H_2 on Pt(111) shows a wide variation with coverage, shifting from an initial desorption onset at low coverages of 400 K to a desorption onset of 250 K at high coverages.[16] We propose that both H_2 desorption peaks are H_2 desorption rate-limited and the origin of the two peaks is a competition between coadsorbates for sites. This competition also affects the benzene TPD spectra, as we will discuss shortly. At low initial coverages of cyclohexadiene, coadsorption of hydrogen with the benzene product results in only a small shift of the H_2 desorption peak to 315 K. However,

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(29) Rodriguez, J. A.; Campbell, C. T. *J. Phys. Chem.* **1989**, *93*, 826.

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at higher initial cyclohexadiene coverages, a more severe competition for sites occurs, destabilizing the adsorbed hydrogen, and the H_2 desorption occurs at lower temperatures. A peak at 280 K results from this destabilization and the benzene desorption at 310 K, which again frees sites and shifts the H_2 desorption to 315 K. This assignment differs from ref 2 which proposes that hydrogen evolution is rate limited by C−H bond cleavage when high initial coverages are used. Unfortunately, this issue cannot be clearly resolved at the present time. BPTDS showed that low coverages of cyclohexadiene dehydrogenated or desorbed by 315 K,[2] but no information is available on the stability of cyclohexadiene at high coverages.

Now we shift our attention to the benzene TPD spectra following cyclohexadiene adsorption on Pt(111). At the lowest coverages investigated, adsorbed benzene is formed on the surface even though no benzene desorption occurs in TPD.[2] The reactivity of the Pt(111) substrate is such that surface-bound benzene is completely decomposed at small benzene coverages. The production of gas-phase benzene at higher initial cyclohexadiene coverages is a consequence of the self-poisoning of the surface by coadsorbed benzene molecules and benzene decomposition fragments. At relatively low coverages, our benzene desorption spectra from the dehydrogenation of cyclohexadiene on Pt(111) nicely reproduce the benzene desorption spectra following benzene dosing on Pt(111).[14] This indicates that these high-temperature benzene TPD peaks formed from the dehydrogenation of cyclohexadiene are benzene desorption rate-limited. At higher coverages, coadsorbed hydrogen destabilizes adsorbed benzene, forcing benzene to desorb in a narrow peak at 310 K. Following H_2 desorption at 315 K, benzene desorption matches benzene desorption spectra following benzene dosing on Pt(111). Surface crowding at high coverages could form a tilted-state of benzene, as was suggested as the source of a sharp, low-temperature desorption peak during TPD studies of this molecule on Pd(111).[31,32] Further evidence for this tilted state was provided from both ARUPS (Angle Resolved Ultraviolet Photoemission Spectroscopy)[33] and NEXAFS (Near Edge X-ray Atomic Fine Structure).[34] Although there are no published accounts of evidence for tilted benzene on Pt(111), Land[35] has reported FTRAIRS (Fourier Transform Reflection/Adsorption Infrared Spectroscopy) data supporting such a hypothesis.

It has been proposed that some cyclohexadiene remains intact to relatively high temperatures at high coverages, and that this accounts for the narrow peak at 310 K in the C_6H_6 TPD spectra.[2] In an autocatalytic process, when sites occupied by benzene and hydrogen are vacated, the remaining cyclohexadiene dehydrogenates and a sharp pulse of benzene desorption occurs. Additional experiments are required to establish this mechanism for several reasons. First, there is no direct evidence of cyclohexadiene at 310 K, and the Pt(111) surface is very reactive, decomposing cyclohexadiene at 230 K at about $^1/_3$ of saturation coverage.[2] Also, the Pt−Sn alloys easily decompose saturation coverages of cyclohexadiene completely below 300 K and these surfaces should be less reactive than Pt(111).

The chemistry of cyclohexadiene on the Pt(111) surface can be compared to that on the two Pt−Sn alloys. The decomposition of benzene that occurs on the Pt(111) surface is completely eliminated on the two Pt−Sn surface alloys.[14] However, there is no observable decrease in the amount of dehydrogenation of cyclohexadiene, and this leads to a huge increase in selectivity to produce gas-phase benzene, especially at low cyclohexadiene coverages.

Cyclohexadiene TPD shows no new desorption peaks with the addition of Sn to the Pt(111) surface. Thus, no reversible chemisorption of cyclohexadiene occurs and complete reaction of the chemisorbed monolayer is observed. The only products observed in TPD are H_2 and benzene. The peak temperatures of the H_2 desorption peaks from cyclohexadiene dehydrogenation on the surface alloys are similar to those seen after H atom adsorption on these surfaces.[16] (H_2 TPD spectra following cyclohexadiene decomposition on the $\sqrt{3}$ alloy only reproduced the low-temperature peak of the two-peak spectrum reported in ref 16 and so it is possible that the high temperature peak was due to a disordered (2×2) alloy phase.) This shows that cyclohexadiene dehydrogenation occurs facilely at low temperatures and that the production of gas-phase H_2 is a H_2 desorption rate-limited process. Both H_2 and benzene desorption, however, show significant change in their desorption spectra compared to those on Pt(111). In both cases increasing the Sn concentration from 0.25 to 0.33 ML causes a reduction in the desorption activation energy of H_2 and C_6H_6. However, it is only by combining the effects of added Sn with a competition mechanism from coadsorbates that we can explain all of the observed phenomena. Note in Figures 6 and 7 that H_2 desorption occurs after the desorption of benzene and we propose that it is the combination of the elimination of sites by Sn atoms combined with an adsorbed H atom site-blocking effect that lowers the benzene desorption energy.

Benzene desorption from cyclohexadiene dehydrogenation on the (2×2) alloy surface, as summarized in Figures 6 and 7, does not occur at the high temperatures (300−500 K) seen in previous studies of benzene adsorption on this alloy.[14] These authors assigned a desorption peak at 280 K to benzene adsorbed on atop sites and a benzene desorption peak at 450 K to benzene adsorbed in 3-fold hollow sites.[13,14] Obviously we have to explain the elimination of the high-temperature benzene desorption peak at 450 K following cyclohexadiene dehydrogenation. The elimination of this peak indicates that the Pt 3-fold sites are blocked. Since H_2 desorbs at higher temperatures than does benzene, coadsorbed H atoms are likely candidates for occupying and blocking the 3-fold hollow sites, thereby forcing the benzene to adsorb only on the atop sites and to desorb at 270 K.

A similar coadsorption effect can be observed on the Pt−Sn $\sqrt{3}$ alloy. Benzene adsorption following cyclohexadiene dehydrogenation is destabilized and desorption occurs at 230 K, compared to 280 K as observed in our previous studies of benzene adsorption on the $\sqrt{3}$ alloy.[14] As on the (2×2) alloy, H_2 desorbs at higher temperatures than C_6H_6 on the $\sqrt{3}$ alloy, pointing to a competition between coadsorbed H adatoms and C_6H_6 molecules which forces the benzene desorption to lower temperature.

The clean Pt(111) surface and the (2×2) alloy both show fairly broad benzene desorption peaks following cyclohexadiene adsorption. In contrast, benzene desorbed from the $\sqrt{3}$ alloy evolves in a single, sharp, low-temperature peak. One possible reason for this unusual desorption peak shape is an autocatalytic process in which benzene is produced and desorbed simultaneously due to coadsorption. BPTDS data set the conversion temperature of 1,3-C_6H_8 to C_6H_6 at ≈230 K on clean Pt(111)[2] which is nearly at the same temperature as the desorption temperature for benzene on the $\sqrt{3}$ alloy. Therefore, conversion of 1,3-C_6H_8 to C_6H_6 and simultaneous C_6H_6 desorption would

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[33] Tysoe; Nyberg; Lambert *Surf. Sci.* **1983**, *135*, 128.

[34] Hoffmann; Zaera; Ormerodl; Lambert; Wang; Tysoe *Surf. Sci.* **1990**, *232*, 259.

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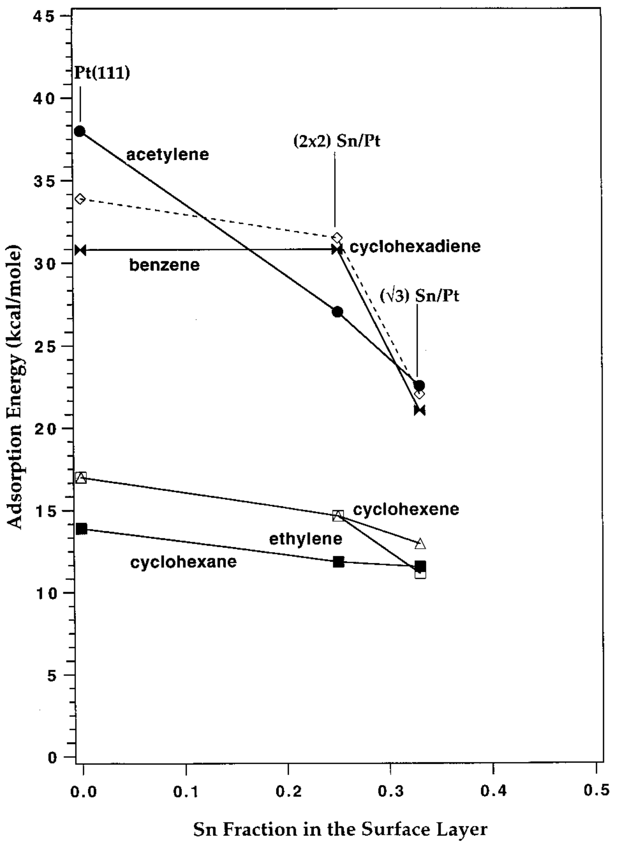

Figure 8. Comparison of the binding energies of alkanes and alkenes on clean Pt(111) and the two Pt−Sn surface alloys. The binding energies for cyclohexadiene were found by first calculating the energy of a quadra-σ bond on clean Pt(111)[36] and then assuming an alkene binding energy dependence on the concentration of Sn. The activation energy for the dehydrogenation of 1,3-cyclohexadiene as found by BPTDS[2] is 13.5 kcal/mol. All other data points were taken directly from Xu et al.[13]

free sites for further conversion and desorption. This autocatalytic process is similar to that proposed by Hugenschmidt et al.[2] as being responsible for the low-temperature benzene desorption peak profile on clean Pt(111).

Next, we consider the bonding of cyclohexadiene to aid the understanding of the reactivity of this molecule on Pt(111) and the two alloy surfaces. HREELS investigations of cyclohexadiene on clean Pt(111) by Hugenschmidt et al.[2] have shown that the molecule was bound to the surface through a quadra-σ-bonding scheme as opposed to the π-bonding scheme seen for benzene.[2] We must consider at this point that the cyclohexadiene molecule may not utilize four Pt−C σ bonds to bind to the Pt−Sn surface alloys. Previously, Xu et al.[13] reasoned that the presence of Sn on the Pt(111) surface decreases the surface-adsorbate bond strength of di-σ-bonded cyclohexene to a greater extent than hydrogen-bonded cyclohexene, and thus, with increased Sn concentration, the hydrogen-bonded species is more strongly bonded on the √3 alloy and thus is the majority species on the surface.[13]

Figure 8 shows a comparison of the desorption energies for several related hydrocarbons, including hydrogen-bonded cyclohexane[13] and di-σ-bonded ethylene.[9]

The adsorption energy for quadra-σ-bonded cyclohexadiene on Pt(111) has been estimated to be 34 kcal/mol by Carter et al.,[36] using a quasiempirical valence bond (QVB) scheme. This places the adsorption energy of cyclohexadiene about midway between the adsorption energy of acetylene and benzene on Pt(111). Comparing the cyclohexadiene desorption energy to the activation energy of 13.5 ± 1.5 kcal/mol (or ≈230 K) that Hugenschmidt et al.[2] found for cyclohexadiene dehydrogenation on clean Pt(111) using BPTDS, it is easy to explain why no cyclohexadiene desorption occurs from Pt(111) prior to the conversion of cyclohexadiene to benzene. Since no chemisorbed cyclohexadiene desorption peaks were observed on the two Pt−Sn surface alloys, we have no experimental measurement of the desorption energy on the alloys. (However, we do know that the activation energy for dehydrogenation is still less than that for desorption.) One can make a very rough estimate of the effect of alloying on the adsorption energy of cyclohexadiene by simply using the influence of alloying on the binding energy for di-σ-bonded cylcohexene. The dashed line shown in Figure 8 crudely estimates the adsorption energy of cyclohexadiene on the two alloy surfaces. Given that no molecular desorption of cyclohexadiene occurs on the two alloys, and the benzene product desorption occurs at 270 K on the (2×2) and 230 K on the √3 alloy, alloying does not reduce the adsorption energy lower than 16.5 kcal/mol on the (2×2) and 14 kcal/mol on the √3 alloy. These activation energies are also upper limits for the activation barriers for cyclohexadiene dehydrogenation on these two alloys and this demonstrates *that alloying Sn with Pt in these surfaces does not appreciably alter the barrier for cyclohexadiene dehydrogenation.*

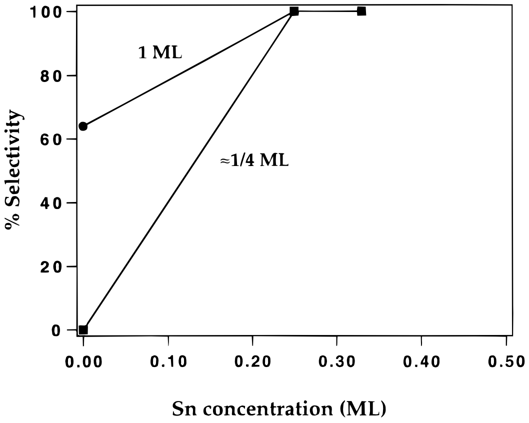

Figure 9. Selectivity plot for Pt(111) and the two surface alloys at submonolayer and saturation coverages. Saturation coverage corresponds to 0.18 molecule of cyclohexadiene per Pt atom. Submonolayer coverage corresponds to 0.05 molecule of cyclohexadiene per Pt atom or about $^1/_4$ saturation coverage. This plot was obtained using the data presented in Figures 6 and 7.

HREELS studies of cyclohexadiene adsorbed on the Sn/Pt(111) surface alloys are obviously needed to determine the nature of the surface−adsorbate bond. Also, Hugenschmidt's[2] earlier study on Pt(111) concluded that 1,4- and 1,3-cyclohexadiene had slightly different dehydrogenation activation energies, and a study of 1,4-cyclohexadiene adsorption and reaction on these alloys might reveal some useful insights into the mechanism of C_6H_8 dehydrogenation.

Finally, we can get some information from our TPD results about the effectiveness of Pt−Sn alloy phases as catalysts for the selective dehydrogenation of cyclohexadiene to benzene. By integrating the peak areas of the H_2 and C_6H_6 TPD curves we can measure activity and selectivity for this reaction. Figure 9 shows the selectivity for the production of gas-phase benzene over the three surfaces during TPD experiments. The selectivity was calculated by determining the ratio of the amount of H_2 produced from the dehydrogenation of C_6H_8 (H_2 desorption below 400 K) divided by the total gas-phase H_2 produced from both C_6H_8 dehydrogenation and C_6H_6 decomposition. Selectivity plots are shown for two coverages, obtained from Figures 6 and 7 for exposures of 0.55 L (≈$^1/_4$ monolayer coverage) and

4.4 L (saturation coverage). The overall reactivity of each surface for cyclohexadiene dehydrogenation during TPD is a constant; no chemisorbed cyclohexadiene desorbs and the saturation monolayer coverage is nearly the same. This can be checked by determining the total quantity of H_2 produced and also by measuring the amount of gas-phase benzene produced. We have made both determinations and obtain consistent results. For example, integration of the benzene desorption curves (after normalization to our TPD curve from a saturation coverage of benzene from benzene dosing) gives benzene yields that agree quantitatively with the selectivities shown in Figure 9 and the relative coverages of cyclohexadiene on the three surfaces. The high reactivity maintained on the alloys for this reaction is in contrast to the reduction in the reactivity of these surfaces for dehydrogenation found in our previous studies of C_2H_2,[10]C_2H_4,[9] C_6H_{10},[13] and C_6H_6.[14] Addition of Sn to the Pt(111) surface increases the quantity of gas-phase C_6H_6 produced and yields a selectivity of 100% for the production of gas-phase benzene from chemisorbed cyclohexadiene on the two alloy surfaces studied. This increased selectivity can be accounted for by combining two phenomena: (i) the elimination of the reaction channel for dehydrogenation of the adsorbed benzene product; and (ii) only weakly inhibiting the dehydrogenation of cyclohexadiene to form adsorbed benzene.

One important consequence of the high selectivity and activity of the cyclohexadiene dehydrogenation reaction on the Pt−Sn surface alloys is that we should be able to carry out a steady state kinetics study of this reaction in UHV. Such a study would be unique for hydrocarbon conversion reactions over metal surfaces and should reveal important insights into the mechanism of this reaction.

2. Comparisons with C_6H_{12}, C_6H_{10}, and C_6H_6 Adsorption and Mechanistic Implications for the Dehydrogenation of Cyclohexane to Benzene. The adsorption and reaction of six-membered cyclic hydrocarbons on Pt(111) and the (2×2) and $\sqrt{3}$ Pt−Sn surface alloys has been a focus of study in our group over the past few years. We have measured how the addition of Sn to the Pt(111) surface changes the binding energy of these adsorbed hydrocarbons and the ability of the surface to activate the C−H bond and dehydrogenate the molecule. Our interest in these molecules arises specifically from our desire to improve the understanding of a prototypical selective dehydrogenation reaction—the conversion of cyclohexane to benzene.

In our previous studies, the monolayer saturation coverages of cyclohexane and cyclohexene were determined by sticking coefficient measurements to be $\approx 0.15 \pm 0.05$ molecules per surface atom, essentially independent of the concentration of Sn.[13,14] We now see that the coverage of the cyclohexadiene molecules on these three surfaces is also not very sensitive to the concentration of Sn alloyed within the surface layer. The monolayer saturation coverage of cyclohexadiene on Pt(111) is 0.18 molecule per surface atom, while it is 0.14 and 0.15 molecule per surface atom on the (2×2) and $\sqrt{3}$ Pt−Sn surface alloys, respectively. The small differences in saturation coverage observed for cyclohexane, cyclohexene, and cyclohexadiene on Pt or the Pt−Sn alloys imply that the *adsorbate saturation coverage is determined essentially by repulsive intermolecular interactions at closest-packing of these molecules on these surfaces rather than indicating the number of contiguous Pt atoms (reactive ensemble size) required for chemisorption*. Also, the reactivity of the alloyed surfaces for chemisorption is much higher than for even low coverages of site blocking adatoms such as Bi on the Pt(111) surface,[17,29,30,37,38] because of the large adatom−adsorbate repulsive interactions within the adlayer which are absent for the alloys.

We can now summarize the influence of Sn on the molecular adsorption energies and C−H bond activation energies of these molecules. A comparison of these numbers reveals insight into the influence of Sn on the selectivity of cyclohexane to benzene conversion reactions. Cyclohexane is H-bonded to the Pt(111) surface[14] with an adsorption energy of 13.7 kcal/mol on Pt(111), 11.6 kcal/mol on the (2×2) Pt−Sn surface alloy, and 11.2 kcal/mol on the $\sqrt{3}$ Pt−Sn surface alloy.[14] The barrier for dehydrogenation of the first C−H bond of cyclohexane was 13.4 ± 1.0 kcal/mol on Pt(111).[39] On Pt(111), there is a close competition between desorption and dehydrogenation paths that leads to partially reversible adsorption and appreciable reaction. However, cyclohexane adsorption on the alloys yielded only molecular cyclohexane and no dehydrogenation products (elimination of benzene production) in TPD studies due to a relatively lower barrier for desorption than reaction.

Cyclohexene is di-σ-bonded to Pt(111)[40] with a desorption activation energy of 17 kcal/mol for Pt(111), 14.6 kcal/mol for the (2×2) Pt−Sn surface alloy, and 12.9 kcal/mol for the $\sqrt{3}$ Pt−Sn surface alloy.[13] The activation energy for cleavage of the first C−H bond to make $C_6H_{9(a)}$ is 14.4 kcal/mole.[40] The Pt(111) surface is very reactive, and at low coverages before self-poisoning becomes a factor, cyclohexene is irreversibly adsorbed and reaction leads largely to carbonaceous species. At higher coverages, where the reactivity of the surface is diminished by coadsorbates, reversible adsorption occurs and the Pt(111) surface shows an appreciable activity for gas-phase benzene production. The Pt−Sn alloys have a lower reactivity than Pt(111), due to an increase in the propensity for reversible adsorption of cyclohexene that arises from the combination of a decrease in the adsorption energy and an increase in the barrier for dehydrogenation. However, due to the elimination of benzene decomposition, these alloys have a higher selectivity for producing gas-phase benzene in TPD compared to Pt(111) at all coverages.[13]

Benzene is strongly chemisorbed on Pt(111) utilizing a π-bonding interaction with the ring plane parallel to the surface plane. Two desorption peaks occur on Pt(111) with energies of 30.8 and 21 kcal/mol.[30] Benzene chemisorption on the (2×2) Pt−Sn surface alloy resulted in the same desorption peaks, but only the lower peak was observed on the $\sqrt{3}$ alloy surface along with a new state at 11.2 kcal/mol.[14] On Pt(111) the activation energy for dissociation of the initial C−H bond is 28 kcal/mol[30] and no dehydrogenation occurs on the alloys.[14] As discussed above for cyclohexene, a competition exists between desorption and dehydrogenation on the Pt(111) surface in which some of the molecules are dehydrogenated and some desorb depending on the benzene coverage. On the two alloy surfaces no dehydrogenation is observed and 100% of the benzene molecules desorb from the surface.

Comparing these results now to cyclohexadiene, we see that cyclohexadiene is a much more reactive molecule on all three surfaces; alloying with Sn does not decrease the activity of the surface for dehydrogenation and does not cause reversible adsorption of cyclohexadiene. Calculations have estimated the adsorption energy of cyclohexadiene on the Pt(111) surface to be $\approx$34 kcal/mol,[36] while the activation energy for C−H bond cleavage is only 14 ± 2 kcal/mol.[2] Sn does not affect the reactivity because of this large difference in the desorption and

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dehydrogenation activation energies. (This of course necessitates that the changes in each due to alloying with Sn do not change the relative energetic positioning of these barriers.) In contrast to all of the other hydrocarbons we have studied, cyclohexadiene is irreversibly adsorbed on all three surfaces for all coverages. The huge increase in selectivity (to 100%) arises from the elimination of benzene decomposition so that all the benzene produced desorbs without decreasing the amount of cyclohexadiene that undergoes dehydrogenation.

A further comment can be made about an important issue concerning the ensemble size requirements for cyclohexadiene dehydrogenation on Pt. The reactive ensemble size (the number of contiguous Pt atoms in a compact arrangement) available on the $\sqrt{3}$ alloy surface to adsorb and dehydrogenate cyclohexadiene is only 2−4 contiguous Pt atoms, assuming Sn is an inert site-blocker. The reactivity that we demonstrate for this alloy surface is much higher than that expected based on past studies of the adsorption and reaction of cyclic hydrocarbons on Pt(111) using preadsorbed Bi adatoms.[17,29,30,39,40] This illustrates that the large ensemble sizes resulting from the sum of the reaction orders for several consecutive elementary steps determined by site-blocking adatoms cannot be simply used to understand alloy chemistry.

A more complete description of the energetics and mechanism for the cyclohexane dehydrogenation to benzene reaction over Pt(111) will be discussed in an upcoming paper.[41] It is clear at this point that the major effect of the addition of Sn to the Pt surface is to reduce the amount of non-selective dehydrogenation of reaction intermediates and of benzene that leads to carbonaceous residue following TPD. This observation, along with the increased selectivity for gas-phase benzene production following the adsorption of benzene and the other reaction intermediates, is consistent with the performance of practical supported Pt−Sn reforming catalysts. This chemistry would be expected if Pt−Sn alloy phases were to play an important role in the catalysis carried out by these commercial Pt−Sn catalysts.

5. Conclusions

We have shown that two Pt−Sn alloys, the p(2×2) and $(\sqrt{3}\times\sqrt{3})R30°$ Sn/Pt(111) surface alloys, show a marked improvement in the selectivity of the dehydrogenation of 1,3-cyclohexadiene (C_6H_8) to yield gas-phase benzene compared to the Pt(111) surface. Furthermore, the reactivity of these alloys is still high enough to cause completely irreversible cyclohexadiene adsorption and carry out dehydrogenation. On the two Pt−Sn alloys, we find a clean, complete conversion of the cyclohexadiene monolayer to form gas-phase benzene during TPD experiments. The addition of Sn to the Pt(111) surface completely suppresses benzene decomposition without significantly inhibiting the dehydrogenation of cyclohexadiene. On all three surfaces, coadsorbed H plays an important role in the reaction kinetics since it effectively competes for sites with coadsorbed benzene and decreases the benzene adsorption bond strength. Furthermore, the activation energy for producing gas-phase benzene over the two alloy surfaces is much lower than on Pt(111). The rate-determining step in this reaction is benzene desorption, and the benzene desorption temperature is lowered on the Pt−Sn alloys compared to Pt(111) due to site-blocking by Sn and coadsorbed H atoms from the dehydrogenation reaction. This gives rise to very fast reaction kinetics on the $\sqrt{3}$ alloy, where the benzene product desorbs at 230 K.

The increased selectivity for production of gas-phase benzene and the complete inhibition of carbon accumulation from cyclohexadiene reaction illustrates the type of improved selectivity and increased resistance to coking of the Sn/Pt(111) surface that one expects if alloys have an important role to play in the improved performance of supported Pt−Sn reforming catalysts.

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